Fig. 2. The spectral changes in the strong, low wavenumber phonons of compressed NH_4Br and ND_4Br powder. The II–V phase transition is observed at 20 kbar and 9 ± 2 kbar at 296 K in NH_4Br and ND_4Br, respectively. The spectrum of ND_4Br II at 1 bar is taken with the sample outside the high pressure cavity.
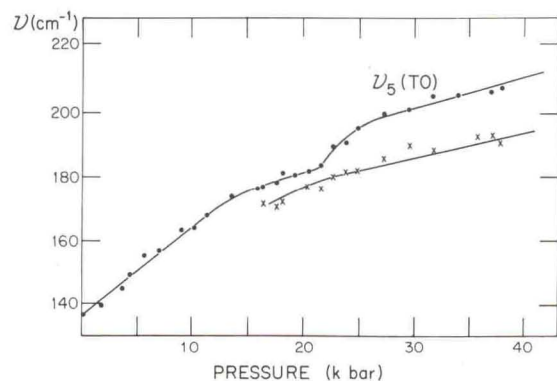

Fig. 3. Plot of wavenumber versus pressure for ν_5 (TO) and the low energy shoulder ν_5'' (B_{2g}) appearing in NH_4Br V.

Fig. 4. The spectra of NH_4Br V are shown at 296 K and 24.5 kbar, 215 K and 4.4 kbar and 200 K and 4.4 kbar. The spectra of phase V is compared to the combined spectra of NH_4Br III (indicated by the dashed line ———) and NH_4Br IV (indicated by the dotted line …) shown in the upper figure. ν_5 (TO) and ν_5 (LO) belong to NH_4Br IV, while ν_7'' (A_{1g}), ν_7' (E_g), ν_5'' (B_{2g}) and ν_5' (E_g) are modes arising from NH_4Br III. The Raman active librational mode, ν_6', arising from NH_4Br III and ν_5 (LO) are only observed at low temperatures in NH_4Br V. At 200 K and 4.4 kbar, for example, ν_6 (E_g) and ν_5 (LO) are located at 338 and 235 cm^{-1}, respectively. The approximate positions of the three modes in the band centered on ν_5 (TO) (indicated by the broken line - - -) are shown in the spectrum of NH_4Br V at 296 K and 24.5 kbar.
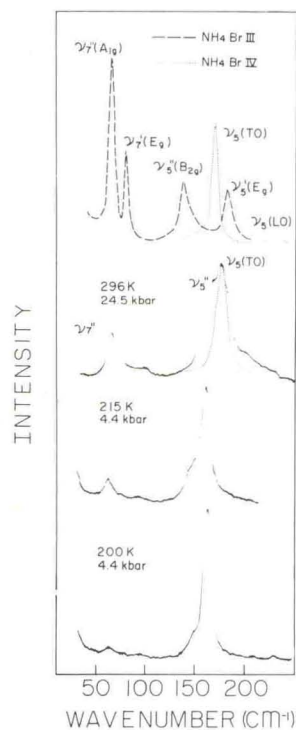

Fig. 4

phonons are conveniently measured by the Grüneisen constants ($\gamma = -\mathrm{d} \ln \nu / \mathrm{d} \ln V$). For the translational motion (ν_5 (TO)) of the NH_4^+ and Br^- sublattices, a large decrease in the γ (from 3.2 to 1.2) is noted upon going from phase II to V, respectively. The spectrum of phase IV (fig. 1, 195 K and 18.6 kbar) consists only of ν_5 and several weak two-phonon bands [2,9]. The above spectroscopic data of NH_4Br V certainly indicates that this phase is formed from the basic CsCl-like units and that the spectra are different from either NH_4Br II or NH_4Br IV.

Raman spectra of compressed NH_4Br powder show the same spectral changes as the single crystal, the II–V phase transition being observed at 20 kbar and 296 K in both cases. Thus, crystal perfection does not affect to a great extent the spectral changes associated with the transition which encouraged the extension of the phase transition studies to powdered ND_4Br. Fig. 2 shows the stronger lattice modes and their variation with pressure in NH_4Br and ND_4Br. Weaker modes which must be located with much wider spectrometer slits are not shown. The lowest frequency mode of the disordered ND_4Br II at 56 cm^{-1} (1 bar and 296 K) shows no measurable isotope effect when compared with the corresponding mode at 56 cm^{-1} of NH_4Br. This 56 cm^{-1} peak can be assigned as the transverse acoustic mode (TA_2) excited at point M of the zone edge with the aid of the published neutron dispersion relation [10]. The spectra of ND_4Br II also shows a broad band at 100–200 cm^{-1} which consists of the strong ν_5 (TO) and a weaker high energy shoulder. Deuteration lowers the II–V transition pressure, the phase boundary being crossed at 9 ± 2 kbar in ND_4Br rather than at 20 kbar and 296 K as in NH_4Br. Fig. 2 reveals that the same characteristic low energy shoulder appears in both ND_4Br and NH_4Br V.

One of the most interesting features of NH_4Br V is the large intensity change of the lattice phonons with variation in temperature and pressure. This intensity variation is in marked contrast to both phase II and IV where only small changes are noted. Qualitatively, the temperature effect on the intensity of NH_4Br V appears to be stronger than the pressure effect, although the two effects cannot be accurately separated and the transmission of the NaCl windows employed in the high pressure cell varies to a small extent. The relative intensities of the low wavenumber peaks in NH_4Br V are seen in fig. 3 at temperatures

ranging from 200 to 296 K. At 296 K and 24.5 kbar, the broad band at 150–250 cm^{-1} consists of a strong central peak at 195 cm^{-1} (ν_5 (TO)) and of low and high energy shoulders at 182 (ν_5'') and 218 cm^{-1} (ν_5'), respectively. The other peaks are located at 78 (ν_7'') and 107 (ν_7') cm^{-1} in NH_4Br V at 296 K and 24.5 kbar. At 5.2 kbar and 200 K, the peaks are located at 63 (ν_7''), 80 (ν_7'), 146 (ν_5''), 160 (ν_5 (TO)), 204 (ν_5'), 235 (ν_5 (LO)) and 335 cm^{-1} (ν_6'). Fig. 3 indicates that there are two classes of peaks, those showing a large decrease (ν_7'', ν_7', ν_5'' and ν_5') and a peak (ν_5 (TO)) characterized by some increase of intensity as the temperature is lowered. The intensity change of the ν_5 (TO) peak with decreasing temperature (296–200 K) cannot be accounted for in terms of one phonon excitation process since an 18% decrease would be expected rather than the observed increase. The large relative intensity decrease with decreasing temperature for the other set of peaks does not follow the intensity behavior of either a one or two phonon process (40–50% decrease). The variation of the intensities of the low energy phonons in NH_4Br V suggests a temperature dependent concentration effect with one set of peaks increasing (ν_5) and the other set (ν_7'', ν_7', ν_5'', ν_5', and ν_6') decreasing with decreasing temperature. The latter set of peaks become Raman inactive at the V–IV transition. The Raman peaks of phase V have similar behaviors in both ammonium bromides with correspondence between 77 to 78 (ν_7''), 167 to 182 (ν_5''), and 178 to 195 cm^{-1} (ν_5 (TO)) at 296 K and 24.5 kbar in ND_4Br and NH_4Br, respectively. The strong intensity variation appears to have led to some confusion in Wang and Wright's interpretation of the spectra of NH_4Br V at low temperature and pressures [11]. These pressure and temperature studies — the agreement of the overall characteristics of the low temperature spectra, especially the isolated peak (ν_7), with those reported by Wang and Wright — and the observation of the same features on the compressed powder and single crystal suggest that the features reported here for NH_4Br V spectra are indicative of this phase [2].

There is no question as to the existence of either the II–V or V–IV transition in ammonium bromide since the changes in the acoustical properties and the spectral changes definitely indicate the transition. The question is the nature of phase V. The Raman data described in this paper can be explained if phase V is